

## WASTE OILS UTILIZED AS COAL LIQUEFACTION SOLVENTS ON DIFFERENT RANKS OF COAL

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### Introduction

Solvent plays an important role in direct coal liquefaction. The solvent acts as a medium to transport hydrogen, as a heat transfer medium, as an additional reactant along with the coal, as a coal dissolution medium, and as the medium to transport coal liquefaction products away from the coal matrix. Recent investigations of coprocessing coal with solid waste materials (plastics, rubbers, cellulose) to raise the hydrogen content of the coal products with a concomitant decreased need for the addition of hydrogen gas have involved reacting solid waste plastics and solid waste rubbers directly with coal with little preparation other than grinding or shredding the waste material.<sup>1-4</sup> (An indirect benefit to coprocessing waste with coal is that less waste must be disposed of in landfills or by incineration.) Dry mixing of coal and waste materials may be the most cost effective method for coprocessing waste with coal because there is less preparation of the waste material. However, the metals, anti oxidants, carbon black, and plasticizers present in the waste materials make some preparation of the reactants necessary. A possible pretreatment of the waste materials would be a vacuum pyrolysis of the waste materials that would produce cleaner oils. To examine this issue, we have recently carried out coal liquefaction experiments in which coals of different ranks were reacted with oils obtained by the vacuum pyrolysis of waste materials, specifically plastics and rubber tires. We have also used waste automotive oils to determine whether the automotive oil is effective, and whether trace heavy metals found in the waste automotive oil can be scavenged by the coal.

### Experimental

Coal samples were obtained from the Penn State Coal Sample Bank. Six different coals were used as received: Pocahontas DECS-19 (low volatile bituminous coal), Blind Canyon DECS-2 (high volatile A bituminous coal), Illinois-6 DECS-2 (high volatile B bituminous coal), Wyodak-Anderson DECS-26 (subbituminous B coal), Smith-Roland DECS-8 (subbituminous C coal), and Buelah DECS-11 (lignite A). Waste automotive crankcase oil was obtained from Book Cliff Energy, Green River, Utah. Oils from the vacuum pyrolysis of waste rubber tires and from waste plastics were obtained from Conrad Industries, Chehalis, Washington. All oils were stored under ambient conditions. All coals were ground to a -60 mesh. Samples were mixed in a 1 part coal to 1 part solvent ratio determined by weight. Each sample was placed in a 27 cm<sup>3</sup> stainless steel tubing reactor with no catalyst. Solvents were stirred prior to being placed in the tubing reactor. Tubing reactors were purged with N<sub>2</sub> and pressurized with H<sub>2</sub> to 1000 psig (cold). Tubing reactors were placed in a sandbath heated to 430 °C and shaken vertically for one hour. The tubing reactor was then removed from the sandbath and allowed to cool for 5 minutes. The tubing reactor was then quenched using cold water. The tubing reactors were left sealed over night. Products were then removed and placed in soxhlet extractor thimbles and extracted with THF. Soxhlet extraction was continued until the extraction solvent appeared clear. The THF was then removed with a rotary evaporator leaving behind the soluble product. The THF soluble product was then dried under vacuum for two hours and weighed. The sum of the THF soluble mass and THF insoluble mass was subtracted from the original coal (daf) weight to account for gas mass. The dried THF soluble portion was then extracted with cyclohexane. The remaining insoluble portion is referred to as asphaltenes and the soluble portion as oil. An effort was made to keep samples under a nitrogen atmosphere in order to minimize air oxidation. GC-MS analyses were completed on a Hewlett Packard 5890 series II Gas Chromatograph coupled to a Hewlett Packard 5971 Mass Spectrometer. A J & W 100 meter long DB-1 column was used for the GC-MS analyses. Trace metals were analyzed by ICP (Data Chem. Laboratories, Salt Lake City, UT).

## Results

The waste automotive crankcase oil from Book Cliff Energy is a mixture of many automotive oils received onsite at their refinery. The vacuum pyrolyzed plastic oil and the vacuum pyrolyzed tire oil from Conrad Industries were prepared from large samples of various plastics and tires. Thus the oils used in this study are representative of those that would be supplied to a coal liquefaction refinery instead of working with oils vacuum pyrolyzed from only one plastic sample or rubber sample.

ICP analysis of the waste automotive oil in Table 1 indicates the presence of many heavy metals. Of specific interest are the high zinc and phosphorous concentrations. This suggests the presence of a lubricant additive identified by Tarrer and coworkers.<sup>5</sup>

ICP analysis of the pyrolyzed plastic oil (Table 1) shows the presence of calcium, iron, and zinc. The calcium arises from the addition of calcium oxide during the pyrolysis of plastic to react with any hydrochloric acid formed from the breakdown of polyvinyl chloride polymers. GC-MS analysis indicates the presence of alkanes as large as C<sub>36</sub>, as well as the presence of cyclic rings, and aromatic species such as benzene and naphthalene.

The ICP results for pyrolyzed tire oil (Table 1) show that zinc is the only heavy metal present. The vacuum pyrolyzed tire oil is low in zinc relative to a standard rubber tire. Past analysis indicates that a rubber tire contains on average 1.5 % by weight zinc oxide. Vacuum pyrolysis of the waste rubber tire circumvents the problems associated with removal of carbon black from the products.<sup>6</sup> Vacuum pyrolysis of waste rubber tires also permits formation of polyaromatics.<sup>7</sup> These polyaromatics are known to be useful in coal reactions because of their hydrogen shuttling and hydrogen donating characteristics.<sup>8,9</sup> Analysis by GC-MS indicated the presence of benzene, methylated forms of benzene, naphthalene, methylated forms of naphthalene, anthracene, methylated forms of anthracene, phenanthrene, methylated forms of phenanthrene, pyrene, methylated forms of pyrene, and naphthacene.

Table 2 contains the product distributions for conversion results obtained from reacting coals of differing ranks with waste oils at 430 °C for 1 hour. It is important to note that the total conversions reported are for the combination of both the coal and the solvent. This appears to be a better way of comparing all three solvent systems because the solvents react differently.

The coals are listed according to rank with Pocahontas being the highest ranking coal used and Buelah being the coal of lowest rank. The Pocahontas coal was not effectively converted using any of the three solvents. This is not surprising since higher rank coals are harder to depolymerize than are lower rank coals. The waste automotive oil solvent and the plastic solvent show similar overall coal rank trends with respect to total conversion. The asphaltene yield was slightly higher for runs using automotive oil solvent than runs using plastic solvent. This is surprising because the plastic oil with its abundance of large alkanes would be expected to increase asphaltene percentages even if larger alkanes did not react with other coal fragments. This indicates some cracking of the plastic solvent during coprocessing. Examination of the reactors indicated some char formation for the plastic solvent whereas no charring was observed for the automotive oil solvent. The lack of charring for the waste automotive oil solvent is what one might predict for an automotive lubricant but increased asphaltenes were not foreseen. It is interesting that trace metals identified in the automotive solvent have no detectable effect in promoting conversion of the coal.

The total conversion yields for the tire solvent indicated no rank correlation in contrast to the automotive oil solvent and the plastic oil solvent. The tire solvent did produce more measurable asphaltenes than did the other two solvents. Visual examination of the tubing reactors revealed enhanced charring with the tire oil present. This is not surprising with char precursors pyrene and anthracene in the initial reaction mixture. These molecules are also known to be beneficial to coal reactions because of their capacity to act as hydrogen donors and shuttlers.<sup>9</sup> The tire oil did not seem to be beneficial for the lower rank coals. The lower rank coals may be too reactive and combine with the solvent to form asphaltenes. The greatest total conversion for all three solvents came from tire oil solvent coprocessed with Illinois #6 coal. The Illinois #6 has a greater proportion of sulfur and iron oxide. These are known to form a sulfided iron which then can act as a catalyst in coal liquefaction. Previous experiments have shown that the pyrolyzed tire oil is beneficial

only in the presence of hydrogenation catalysts. It may be that the hydrogenation catalyst partially hydrogenated the pyrolyzed tire oil which could then act as a hydrogen donor.<sup>10</sup>

The ICP analyses for metals in the product oils for the three solvents coprocessed with the six different coals are shown in Table 3. The ICP analysis shown in Table 1 for the automotive oil solvent before it was coprocessed with any coal is also presented at the far right hand column of the Table in order to compare the amount of metal present in products derived from three coal/solvent distributions. Table 3 shows a decrease in almost every metal detected in the original solvent. A substantial decrease is observed for zinc, phosphorous, magnesium, iron, copper, barium, and aluminum. Tarrer and coworkers have indicated that the high content of zinc and phosphorous is due to the presence of zinc dialkyldithiophosphate.<sup>5</sup> It appears that the oils produced from the Illinois #6 coal and the Wyodak-Smith coal are the cleanest overall with respect to trace heavy metals.

The results from oils and asphaltene indicate that no one coal is significantly more efficient than the others at capturing heavy metals. Therefore, it is difficult to say if there is any rank effect correlation for capturing heavy metals. The data appear to indicate that all coals have to some degree an ability to capture heavy metals. It is possible that the heavy metals in the automotive oil solvent were not plentiful enough to saturate the scavenging abilities of the coals in order to determine which coal would be the best scavenger. This scavenging or capture may involve the chemistry of the coal or a physical effect of incorporating the heavy metals into the carbon matrix of the coal. In past studies<sup>11</sup> using Electron Probe Microanalysis (EPMA), heavy metals were observed to reside in coal particles after coprocessing coal with waste rubber tires. In the EPMA micrographs the area of high heavy metal localization also coincided with areas of high sulfur concentration indicating that metals were present as sulfides. Therefore, sulfur in the coal may be beneficial for scavenging. This was also reported by Tarrer and associates for work completed on scavenging of zinc dialkyldithiophosphate. They found the scavenged zinc from the automotive oil residing in coal in the form of zinc sulfide. The ultimate analysis shows that the Illinois #6 has an abundant amount of sulfur. Illinois #6, along with the Wyodak-Anderson appeared to localize trace metals only slightly better than the other metals according to Table 3.

### **Conclusion**

The Pocahontas coal is not a good coal to be coprocessed with any waste oil solvent to produce liquid transportation fuels. The other coals showed similar conversions with waste oil solvents except the Illinois #6. Results for different coal ranks liquefied in different solvents indicate that the Illinois #6 gives the best total conversion when reacted with oil derived from the vacuum pyrolysis of waste rubber tires. As for the heavy metals in waste automotive oils, coprocessing the automotive oils with the coal diminishes the amount of metal found in the products. Scavenging of metal did not appear to be coal rank dependent under the experimental conditions used in this study.

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Table 1 ICP Analysis of Automotive Solvent, Pyrolyzed Plastic Solvent, and Pyrolyzed Tire Solvent

Metal	Automobile Oil Solvent µg/g	Pyrolyzed Plastic Oil Solvent µg/g	Pyrolyzed Tire Oil Solvent µg/g
Aluminum	81		
Antimony			
Arsenic			
Barium	9.3		
Beryllium			
Cadmium	1.4		
Calcium	920	520	
Chromium	1.7		
Cobalt			
Copper	54		
Iron	310	50	
Lead	27		
Lithium			
Magnesium	240		
Manganese	7		
Molybdenum			
Nickel	13		
Phosphorous	870		
Potassium	510		
Selenium	1.3		
Sodium	34		
Silver			
Strontium	2.7		
Thallium			
Vanadium			
Zinc	850	20	40

Blank areas indicate that none of the element was detected

Table 2 Comparison of Total Conversions (Percent by Weight) for Coals of Different Coal Rank Coprocessed With Waste Oils at 430 °C for 1 Hour

	Automotive Oil Solvent	Pyrolyzed Plastic Oil Solvent	Pyrolyzed Tire Oil Solvent
<b>Pocahontas</b>			
Gas + Oil	54.5	54.3	47.0
Asphaltenes	2.4	0.5	9.0
Total Conversion	56.9	54.8	56.0
<b>Blind Canyon</b>			
Gas + Oil	65.4	66.5	60.4
Asphaltenes	3.7	3.6	10.3
Total Conversion	69.1	70.1	70.7
<b>Illinois #6</b>			
Gas + Oil	66.1	64.4	65.8
Asphaltenes	10.4	7.2	17.8
Total Conversion	76.5	71.6	83.6
<b>Wyodak</b>			
Gas + Oil	70.2	71.5	63.1
Asphaltenes	3.7	1.4	5.1
Total Conversion	74.0	72.9	68.3
<b>Smith - Roland</b>			
Gas + Oil	74.8	73.4	67.9
Asphaltenes	3.2	1.4	4.8
Total Conversion	77.9	74.7	72.7
<b>Beulah</b>			
Gas + Oil	74.2	77.2	66.1
Asphaltenes	2.0	0.4	3.8
Total Conversion	76.2	77.6	69.9

Table 3 Comparison of ICP Analyses of Oils Produced From Coal and Waste Automotive Oil Solvent Coprocessed at 430 °C for 1 Hour

Oil	Pocah.	Blind Canyon	Illinois #6	Wyod.-And.	Smith-Roland	Beulah	Auto Oil
Aluminum							81
Antimony							
Arsenic					31		
Barium							9.3
Beryllium							
Cadmium		1.2		0.9			1.4
Calcium	260	56	42	51	64	200	920
Chromium	1.1	1.4			3.4	2.5	1.7
Cobalt						10	
Copper		2.2			7.4		54
Iron	23	62	19	77	42	45	310
Lead							27
Lithium					3.4		
magnesium							240
Manganese							7
Molybdenum							
Nickel	11	10		6.2	16		13
Phosphorous							870
Potassium	690	400	470		770	340	510
Selenium	31						1.3
Silver					1.3	1.3	34
Sodium		400					
Strontium							2.7
Thallium							
Vanadium							
Zinc	15	14	8	11	15	11	850